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Jamming and Crystallization of Polymeric Micelles

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Polymeric micelles formed by hydrophobically end-capped poly(ethylene oxide) (PEO) copolymers in water show a discontinuous liquid-solid transition, which occurs above a critical concentration that increases with increasing temperature. The solid state contains a body-centered cubic phase in equilibrium with a disordered phase. The fraction of crystalline phase increases with increasing concentration and decreasing temperature. A comparison of the structure and the rheology during cooling shows that the micelles jam before the ordered phase is formed. The discontinuous liquid-solid transition and the distinct bcc phase over a wide range of concentrations are not observed for true star polymers. The difference is perhaps due to the adjustment of the number of arms in the case of close packed polymeric micelles.

Polymeric micelles are formed by the association of block copolymers with a relatively small insoluble block. They show an abrupt transition from a free-flowing liquid to solid-like behaviour above a critical concentration or below a critical temperature. Generally, liquid crystalline order is observed in the solid state. The coincidence between the liquid-solid transition and the appearance of liquid crystalline order has induced some authors to conclude that the solidification is a result of micelle ordering. The objective of our work was to investigate in more detail the correspondence between the liquid-solid transition and the formation of the ordered phase.

We studied poly(ethylene oxide) (PEO) with a molar mass of 4500 g/mol that was end-capped with octadecyl. In water, this polymer forms micelles containing 24 chains. With increasing polymer concentration, the viscosity increases similarly to that observed for equivalent star polymers. However, above a critical concentration that increases with increasing temperature, a discontinuous transition is observed and PEO goes from a viscous liquid to a solid that does not flow when the sample is tilted. The transition, which can also be observed by cooling the sample at a fixed concentration, is fast at temperatures far below the critical value, but can take more than 10 hours just below the critical temperature.

Small-angle x-ray scattering (SAXS) shows narrow Bragg peaks in the solid state, indicating a body-centred cubic phase. However, the amplitude of the peaks is very small when the sample is close to the transition and becomes progressively larger with increasing concentration or decreasing temperature. The underlying amorphous structure can still be clearly distinguished, showing that the solid contains both a crystalline and a disordered phase in equilibrium. The position of the Bragg peaks is independent of the temperature, but shifts to lower scattering wave vectors with increasing concentration. The concentration dependence of the peak position shows that the aggregation number of the micelles in the solid state increases with increasing concentration.

Figure 1 shows, for the same concentration (300 g/L), a comparison of the variation of the shear modulus and the structure factor during a cooling ramp. It is clear that the liquid-solid transition occurs at a higher temperature than the formation of the bcc phase, even though the cooling rate was much faster

for the shear measurement. This implies that the crystalline phase is formed only after the micelles have jammed and, thus, that the formation of the ordered structure is not the origin of the liquid-solid transition.

Polymeric micelles resemble multi-arm star polymers and their behavior is similar at low-volume fractions. The viscosity of true star polymer solutions increases steeply above the overlap concentration, but the increase is continuous. In addition, liquid crystalline order is rarely, and only with difficulty, observed for concentrated star polymers. The essential difference between star polymers and polymeric micelles is that in the latter case the number of arms is variable, which gives the system an extra degree of freedom to minimize the free energy. This is probably the origin of the observed differences.

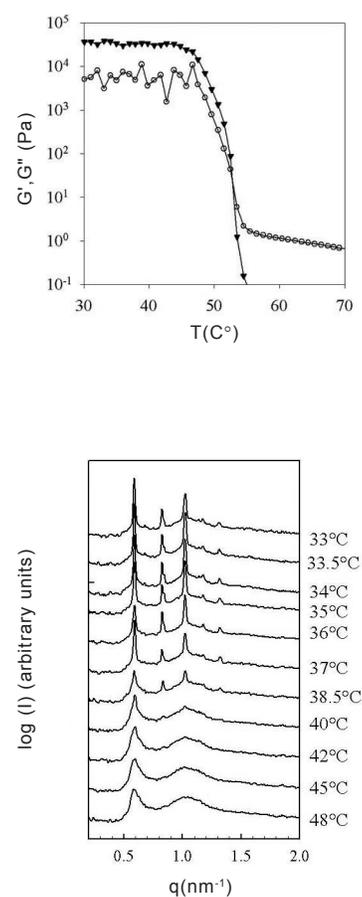


Figure 1. Comparison of the evolution of the shear moduli (top) and the SAXS spectra (bottom) during cooling for suspensions of polymeric micelles at 300g/L. The cooling rate for the rheology experiment was faster (5 degrees/min) than for the SAXS experiment (less than 1 degree/min).